

New Science with the LERIX spectrometer at the Advanced Photon Source

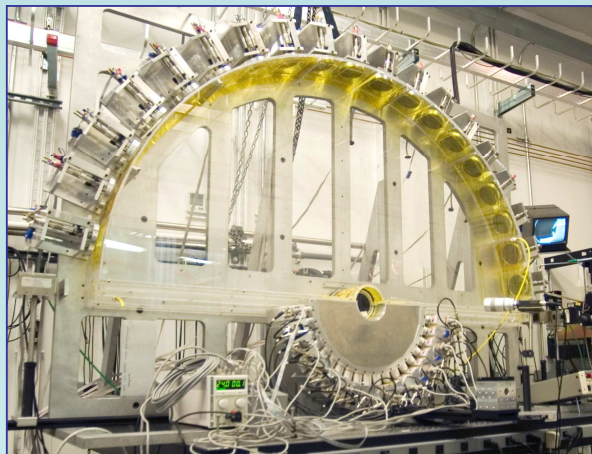
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The LERIX (lower-energy resolution inelastic x-ray scattering) spectrometer is a new APS user facility for measurement of momentum-transfer dependent (q) x-ray Raman scattering (XRS).¹ Our goal: a user-friendly, high-throughput facility to use hard x-rays for bulk-sensitive measurement of $S(q, \omega)$ in the UV and soft x-ray energy range with the added option of non-dipole selection rules. These selection rules arise from the multipole terms in the expansion of the dynamic structure factor $S(q, \omega)$:

$$S(\vec{q}, \omega) = \sum_f \left| \langle f | e^{i\vec{q} \cdot \vec{r}} | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$$

$$= \sum_f \left| \langle f | 1 + i\vec{q} \cdot \vec{r} + \frac{(\vec{q} \cdot \vec{r})^2}{2} + \dots | i \rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$$

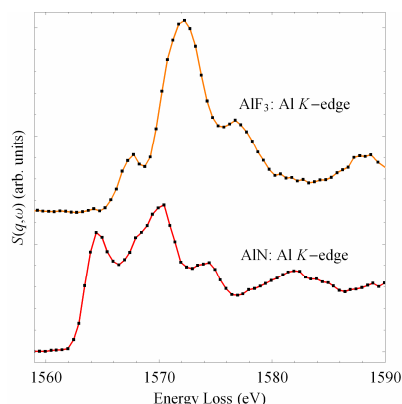
1. T.T. Fister, G.T. Seidler *et al* RSI 77 p. 063901 (2006)



LERIX studies to date include:

- B₄C materials for industrial applications
- Carboranes: tunable selection rules
- Amine boranes and LiH for H-storage
- Battery applications: Li-intercalated graphite, metal oxides
- Carbon aerogels for supercapacitor and battery electrodes
- Carbon nano-onions (nanostuff in space?)
- Petrochemicals: coal and extract from coal shale
- Intermediate-range fine structure in ice at O K-edge
- Mg and Al L-edges: Background proportional enhancement of XRS (also K-edges)
- AlN, SiC: LED applications (all edges)
- AlF₃ Lewis-acids (all edges)
- Exciton spectroscopy in alkali halides (NaF, LiF, ...)
- Transition metal oxides: metal L-, M-edges & O K-edge
- CeO₂, CeRh₃, ... O K-edge and XUV low-energy edges in f-electron systems
- Future: solution studies, chem. reactor studies, "low-pressure" capabilities, actinide compounds

Dipole limit: signal proportional to μ in x-ray absorption



Tightly bound initial states, such as the above Al K-edges from AlF₃ and AlN, do not typically have much q -dependence; hence, LERIX can integrate over all 19 channels in q for increased count rates. For instance, each of these measurements only took a couple hours!

Dipole-forbidden transitions: measure the final states' symmetry, i.e. the I -DOS.

We can expand $S(q, \omega)$ in terms of the I -DOS, $\rho_i(\omega)$, with each term weighted by an atomic coefficient M_i :

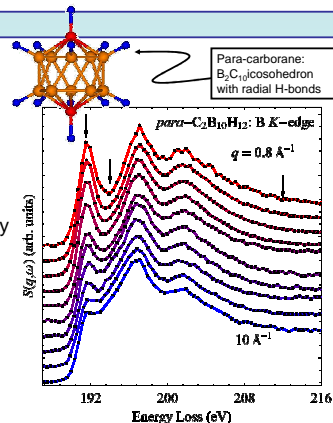
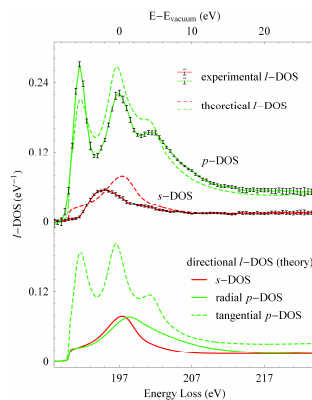
$$S(q, \omega) = \sum (2l+1) |M_i(q, \omega)|^2 \rho_i(\omega)$$

For C₂B₁₀H₁₂, we find that only the s - and p -DOS significantly contributed to $S(q, \omega)$. At each energy we then have:

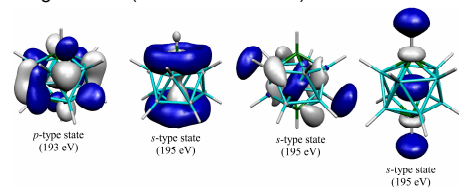
$$S(q_1, \omega_1) = M_0^2(q_1, \omega_1) \rho_0(\omega_1) + 3M_1^2(q_1, \omega_1) \rho_1(\omega_1)$$

$$\vdots = \vdots$$

$$S(q_{10}, \omega_1) = M_0^2(q_{10}, \omega_1) \rho_0(\omega_1) + 3M_1^2(q_{10}, \omega_1) \rho_1(\omega_1)$$



This is an overdetermined set of linear equations and can be inverted for an experimental measure of the I -DOS, as shown on the left. By separating the directional components of the I -DOS, we show that the measured hybridization of the I -DOS agree with prior predictions of s - p radial and p -type tangential antibonding orbitals. (DFT orbitals below)



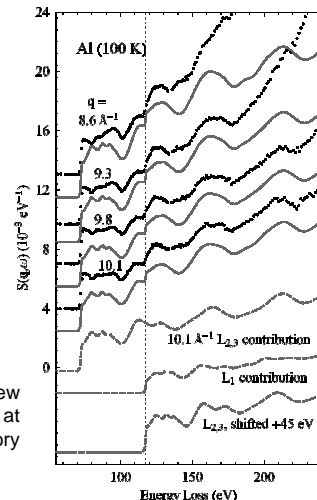
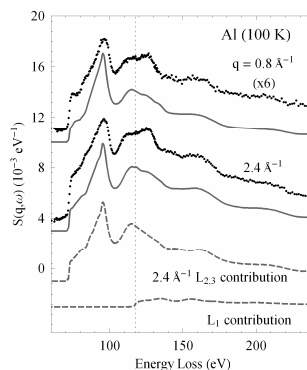
Background proportional enhancement of fine structure at high q for low-energy edges

Like x-ray absorption spectroscopy (XAS), we can express $S(q, \omega)$ in terms of an atomic background, S_0 , with an additional fine structure term, χ .

$$\mu(\omega) = \mu_0(\omega) [1 + \chi(\omega)] \quad S(\vec{q}, \omega) = S_0(\vec{q}, \omega) [1 + \chi(\vec{q}, \omega)]$$

In XAS, χ is the quantity of interest: it represents the interference between the excited photoelectron and backscattering from surrounding atoms. Since μ_0 is a decreasing function in XAS with energy, the measured amplitude of the fine structure is similarly reduced. In XRS, the atomic background can actually *increase* with energy at higher q . As a result, extended fine structure can actually be enhanced using XRS, as can be seen in comparing the low- q and high- q results for Al on the right.¹

Using previously developed *ab initio* multiple scattering theory for XAS, Soininen, Ankudinov, and Rehr have developed a new approach for calculating q -dependent XRS spectra.² As shown in the two figures, this theory is especially successful at extended energies. Note that contributions from the valence inelastic x-ray scattering cause the separation between the theory and experiment at 8.6 and 9.3 Å⁻¹.



1. T.T. Fister, G.T. Seidler *et al* PRB 74 p. 214117 (2006); 2. J.A. Soininen *et al* PRB 72 p. 45136 (2005)